

Copolyester Sequence Distribution by 60, 100, and 220 MHz PMR

E. V. GOUINLOCK,* R. A. WOLFE, and J. C. ROSENFELD, *Hooker Research Center, Hooker Chemicals & Plastics Corp., Niagara Falls, New York 14302*

Synopsis

The proton magnetic resonance spectra at frequencies of 60, 100, and 220 MHz of two bisphenol A-neopentyl glycol-terephthalate copolyesters having the same overall composition but different sequence distributions are correlated. Analysis of the terephthalate proton resonances indicates the usual singlets for the two symmetrical diester sequences. However, the dissimilar protons in the unsymmetrical diester give rise to an apparent quartet originating from an incompletely resolved AA'BB' spectrum. The apparent quartet coupling constant is accurately determined to be 8.03 Hz by a 220 MHz separation of the appropriate peaks and is found to be approximately 8.3 Hz by employing a shift reagent [Pr(fod)₃] in conjunction with suitable model compounds at 100 MHz. This permits an approximate calculation of the entire quartet intensity in those cases where the outside resonances of the latter and the singlets are superimposed, resulting in a more accurate calculation of sequence distribution. In particular, a copolyester prepared by a normal two-stage, interfacial polycondensation yields a degree of randomness *B* estimated to be slightly greater than 1, indicating a nearly random distribution of the comonomers. A second copolyester, prepared so as to enhance an alternating comonomer sequence, exhibits a *B* value of about 1.85.

INTRODUCTION

High-resolution nuclear magnetic resonance spectroscopy elucidates monomer sequence order and steric placement in vinyl copolymers.¹ Although such polymers have received the major emphasis, condensation polymers, particularly copolyesters, have been examined by proton measurements. However, studies have apparently been limited to determinations at a frequency of 60 MHz.

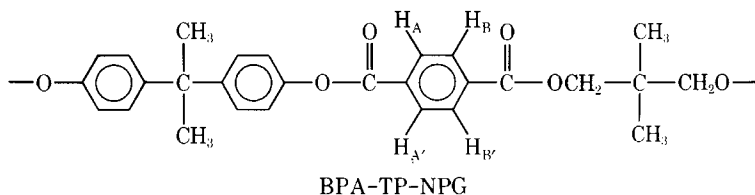
Yamadera and Murano² and Khramova et al.,³ following the initial investigations of Harada and Ueda,⁴ have examined several copolyesters, particularly those from ethylene glycol and a mixture of two dibasic acids. The chemical shifts for the aliphatic (glycol) protons reflect the sequence of the (acid) monomers. At 60 MHz, three singlet resonance peaks, corresponding to the two symmetrical and one unsymmetrical diester sequences, are observed. The intensities of these singlets allow a determination of the degree of randomness (*B*) and of the average sequence length.

* Present address: Polymer Science and Engineering Dept., University of Massachusetts, Amherst, Massachusetts 01002

Hamb⁵ and Korshak et al.⁶ have applied this approach to copolyesters composed of a single dibasic acid (terephthalate) and two diols (a bisphenol and an aliphatic glycol). In this case, observation of the terephthalate protons resonance peaks provides the sequence information.

In the above studies, the unsymmetrical diester sequence gives rise to glycol or terephthalate protons which are dissimilar. However, fine splitting (coupling) of these nuclei has not been observed. Specifically, Korshak et al.⁶ report a single peak for a perfectly alternating copolyester.

The present study concerns a copolyester from 2,2-bis(4-hydroxyphenyl)propane (BPA), neopentyl glycol (NPG), and terephthaloyl chloride (TPC).⁷ The diols are present in equimolar amounts. The unsymmetrical sequence has the structure



Two copolyesters, each prepared by a two-step polycondensation but possessing different sequence distributions, are examined by 60, 100, and 220 MHz PMR. Coupling of the dissimilar terephthalate protons (H_A and H_B above) is found for the unsymmetrical sequence, leading to the observation of an apparent resonance quartet.

EXPERIMENTAL

The PMR spectra were obtained on Varian Associates spectrometers T-60, HA-100, and HR-220 at room temperature (ca. 18° at 220 MHz) at a concentration of about 8% (w/w) in $CDCl_3$, employing tetramethylsilane, assigned a resonance position of zero ppm (δ scale), as the internal reference. (The 220 MHz spectrum was provided by A. Grey of the Ontario Research Foundation, Canada.) Following the separation of the resonance peaks as indicated on the spectra (see below), integrated intensities were obtained by polar planimeter on suitably scale expanded spectra (sweep widths of 100 and 250 Hz).

Copolyester 1 was prepared by a two-step condensation. TPC (1 mole) was reacted with NPG (0.5 moles) at 100°C, and the product, dissolved in methylene chloride, was reacted interfacially at room temperature with an aqueous sodium hydroxide solution of BPA (0.5 moles) in the presence of a quaternary ammonium chloride as catalyst. Copolyester 2 was similarly prepared except that 10 moles of TPC were used in the initial step in order to enhance the ultimate content of the unsymmetrical diester sequence, the excess diacid chloride being removed at 100°C under vacuum prior to the subsequent interfacial polycondensation.

The thoroughly water-washed and precipitated copolyesters have intrinsic viscosities (in 1,1,2,2-tetrachloroethane at 30°C) of 0.77 and 1.61 dl/g, respectively.

RESULTS AND DISCUSSION

Preliminary 100 MHz Spectra

Preliminary (100 MHz) spectra were obtained for various BPA-NPG-TP copolyesters, for NPG-TP and BPA-TP homopolymers, and for the low molecular weight model compounds diphenyl terephthalate, dimethyl terephthalate, and a mixture of these two compounds with methylphenyl terephthalate (molar ratios are 1/1/1.5). The observed terephthalate proton chemical shifts are identical within experimental error for the methyl and the neopentyl esters and for the BPA and the phenyl esters. Four resonance peaks, qualitatively similar to Figure 2, with the following diester assignments are observed:

Sequence	Designation	ppm (δ)
BPA-TP-BPA	S_1	8.28 ± 0.02
BPA-TP-NPG	{quartet-2	8.20 ± 0.01
	{quartet-3	8.16 ± 0.01
NPG-TP-NPG	S_2	8.06 ± 0.02

In the case of the unsymmetrical sequence, the terephthalate protons, since they occur in a para-disubstituted benzene ring, are expected to give rise to a four spin spectrum of the AA'BB' type.⁸ This anticipated spectrum is actually observed as a quartet (see Fig. 3) due to a lack of resolution which is characteristic of polymer spectra. However, the apparent quartet may be used to a reasonable approximation to interpret the results. The peaks at 8.20 and 8.16 ppm are necessarily the 2 and 3 peaks of this quartet. The 1 and 4 quartet peaks are found at positions at 100 MHz which superimpose with the singlets at 8.28 and 8.06 ppm.

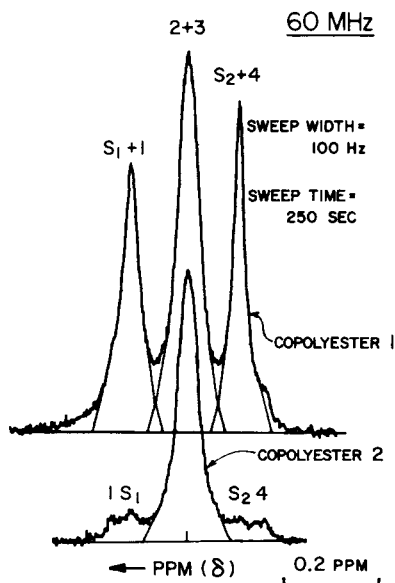


Fig. 1. 60 MHz spectra of copolyesters 1 and 2.

Figure 3 includes an indication of the quartet peak spacings. Peaks 1 and 2 are due to terephthalate protons A and peaks 3 and 4 to protons B. The coupling constant J , given by $\nu_1 - \nu_2 = \nu_3 - \nu_4$, is actually the sum of the ortho and para pair separations, $J_{AB} + J_{AB}'$. The chemical shift $\Delta\nu$ between the geometric mean of peaks 1 and 2 and the mean of peaks 3 and 4, expressed in frequency (Hz) units, depends upon the strength of the magnetic field. However, J , in Hz units, is not field dependent. Therefore, measurements at 60 and 220 MHz, discussed below, separate the singlet and outside quartet peaks which are superimposed at 100 MHz.

Copolyester Spectra

For the two copolyesters, the 60, 100, and 220 MHz spectra, each covering the ppm range of about 8.0–8.4 δ , are shown in Figures 1, 2, and 3, respectively. (The copolyester 1 spectrum at 220 MHz was not determined.) Figure 4 compares these spectra on a frequency (Hz) scale, but also indicates the chemical shifts in ppm for the various resonance peaks.

At 60 MHz, copolyester 1 displays three peaks, as has been observed for similar polyesters at this field strength by Hamb⁵ and by Korshak et al.⁶ In contrast, copolyester 2 exhibits five peaks, although the peripheral reso-

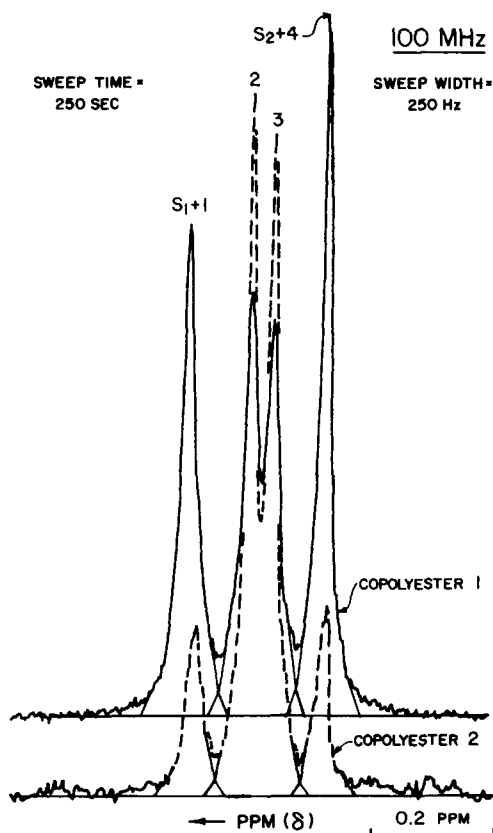


Fig. 2. 100 MHz spectra of copolyesters 1 and 2.

nances are weak and poorly resolved. The center peak in these spectra may be assigned to an unresolved superposition of the 2 and 3 quartet peaks. The 1 and 4 quartet peaks are resolved with respect to the singlets in the copolyester 2 spectrum due to the relatively low intensity of the latter resonances (see Fig. 4). However, their quantitative measurement is not feasible.

At 100 MHz, the 2 and 3 quartet peaks are well resolved for both copolyesters, but in each case the outside quartet peaks and the singlets are superimposed due to a close correspondence between the singlet chemical shifts and the coupling constant at this field strength. Consequently, a total of four peaks are found for each copolyester.

At 220 MHz, copolyester 2 exhibits each of the six anticipated peaks. However, the 2 and 3 quartet peaks are not as well separated from the 1 and 4 resonances as in the case of the 60 and 100 MHz spectra.

Quartet Coupling Constant

The average coupling constant found from the 220 MHz spectrum (Fig. 3), on replicate determinations, is 8.03 ± 0.04 Hz. At 100 MHz, the quartet and two singlets are also directly observed for the mixture of diphenyl, dimethyl, and methylphenyl terephthalate in the presence of a lanthanide shift reagent $[\text{Pr}(\text{fod})_3]$, as shown in Figure 5. In this spectrum, some overlap of BPA aromatic protons with the NPG-TP-NPG singlet occurs. (If an actual copo-

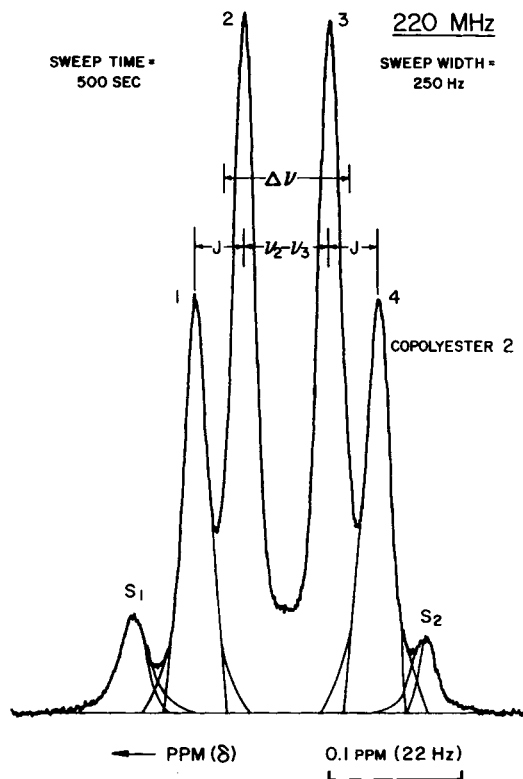


Fig. 3. 220 MHz spectrum of copolyester 2.

lyester, no. 1, was substituted for the model compound mixture, a sufficiently resolved spectrum was not obtained.) Scale-expanded 100 MHz spectra (not shown) were obtained for the same model compound mixture at a concentration of 5.6% and shift reagent concentrations of 1.4 and 3.2% (all w/w). The coupling constant observed, ca. 8.3 Hz, is independent within experimental error of the shift reagent concentration and in reasonable agreement with the copolyester value determined at 220 MHz without shift reagent (8.03 Hz).

Peak assignments in Figures 1–3 (see Fig. 4) are found to be consistent with the observed coupling constant and with the required chemical shifts for the two singlets. Where an apparent discrepancy in J occurs (see, particularly, copolyester 1 at 60 MHz in Fig. 4), it is due to the dominant influence of the singlets on the location of the $S_1 + 1$ and $S_2 + 4$ peaks.

Degrees of Randomness

Degree of randomness B is calculated from the contents of the three possible diester sequences (diads), the latter being derived from the intensities of

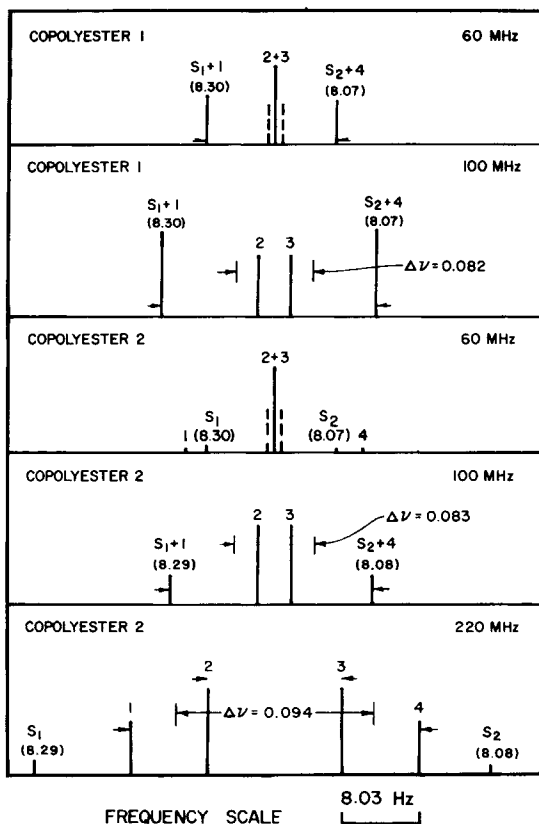


Fig. 4. 60, 100, and 220 MHz spectra of copolyesters 1 and 2 on a frequency scale. The arrows indicate the calculated intensities [eq. (2)] of quartet peaks 1 and 4. Chemical shifts in ppm (δ) are shown in parentheses (below the peak assignments). $\Delta\nu$ values (in ppm) calculated using $J = 8.03$ and observed $\nu_2 - \nu_3$ values (Table I). Peaks shown as dashed lines are calculated quartet 2 and 3 peaks (see footnote a, Table I).

the six resonances. For the copolyester composition considered, with the diols present in equal molar amounts, and following the treatment of Yamadera and Murano,²

$$B = 2P_{NB} = 2P_{BN} = 2A_{BN(1-4)}, \quad (1)$$

where P_{NB} is the probability of a NPG ester group being followed by a BPA, P_{BN} is the probability of the reverse sequence, and $A_{BN(1-4)}$ is the fractional intensity of quartet peaks 1, 2, 3, and 4. For a random polyester, $P_{BN} = A_{BN(1-4)} = 0.5$, and for a perfectly alternating polymer, $P_{BN} = A_{BN(1-4)} = 1$. The respective B values are, therefore, 1 and 2. Intermediate B values correspond to copolyesters containing more alternating placements than dictated by random statistics.

In cases where the 1 and 4 quartet peaks are not directly observed, their intensity may be approximated by the well known AB quartet relation⁸

$$\frac{i_1}{i_2} = \frac{i_4}{i_3} = \frac{\nu_2 - \nu_3}{2J + (\nu_2 - \nu_3)} \quad (2)$$

where i is the intensity of the subscripted resonance, and J , as noted above, is defined as $\nu_1 - \nu_2 = \nu_3 - \nu_4$. If $A_{BN(2-3)}$ is the experimentally observed fractional intensity of the 2 and 3 peaks, it may readily be shown from equation (1) that

$$B = 2A_{BN(2-3)} \left(1 + \frac{i_1}{i_2} \right). \quad (3)$$

Table I includes the B values for the copolyesters at each of the NMR frequencies studied based on the directly measured $A_{BN(2-3)}$ and/or $A_{BN(1-4)}$ values.

For copolyester 2 at 60 and 100 MHz, degrees of randomness B of 1.74 and 1.73, respectively, are calculated indirectly from eq. (3) using the observed $A_{BN(2-3)}$ values and the i_1/i_2 ratios calculated from eq. (2).

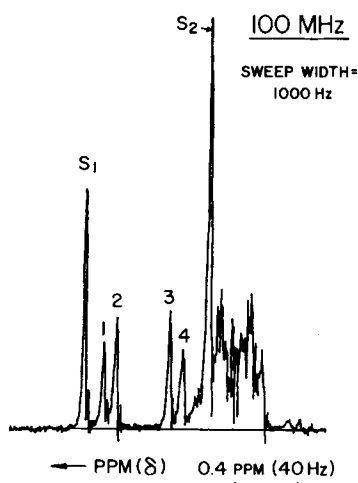


Fig. 5. 100 MHz spectrum of mixture of diphenyl, dimethyl, and methylphenyl terephthalate (molar ratios are 1/1/1.5) in presence of $\text{Pr}(\text{fod})_3$.

TABLE I
 Degrees of Randomness

Copolyester	NMR frequency, MHz	$\nu_2 - \nu_3$, Hz	i_1/i_2 ^b	Observed $A_{BN}(2-3)$	B^c	Observed $A_{BN}(1-4)$	B^d
2	60	1.52 ^a	0.087	0.800	1.74	—	—
	100	3.52	0.180	0.734	1.73	—	—
	220	14.1	0.468 ^e	0.59 ± 0.02	1.73 ± 0.06	0.915-0.93	1.83-1.86
1	60	1.52 ^a	0.087	0.461	1.00	—	—
	100	3.44	0.176	0.416	0.98	—	—

^a Calculated using $J = 8.03$ Hz and $\Delta\nu = 0.086$ ppm and $\Delta\nu = [(\nu_1 - \nu_4)(\nu_2 - \nu_3)]^{1/2}$.

^b Calculated from eq. (2) using $J = 8.03$.

^c Calculated from eq. (3) and i_1/i_2 values calculated from eq. (2).

^d Calculated from eq. (1).

^e The i_1/i_2 directly observed is 0.57 ± 0.04 ; the corresponding $A_{BN}(2-3)$ is 0.59 ± 0.02 .

For this copolyester at 220 MHz, sequence distribution may be derived indirectly, as above, or directly from the observed $A_{BN(1-4)}$ value and eq. (1). By the latter approach, B is found to be 1.83–1.86, the exact value depending on the particular separation assumed between the two (somewhat unequal intensity) singlets and the quartet (see Fig. 3).

$A_{BN(2-3)}$ and i_1/i_2 for copolyester 2 at 220 MHz are not precisely determined by direct observation owing to limited peak resolution (see Fig. 3). However, values of 0.59 ± 0.02 and 0.57 ± 0.04 , respectively, are obtained using the particular range of peak separations shown in Figure 3 and the maximum value of $A_{BN(1-4)}$. The B value derived from this $A_{BN(2-3)}$ value by the indirect calculation is 1.73 ± 0.06 , in agreement, as would be expected, with the 60 and 100 MHz results.

The 7% disparity between the directly and indirectly calculated B values (1.86 vs. 1.73) is a consequence of the difference between the observed and calculated i_1/i_2 values (0.57 vs. 0.468). Thus, eq. (2) is seen to underestimate the intensities of the outside quartet peaks, and the value of 1.83–1.86 may be considered to be the more accurate estimate for B .

In the case of copolyester 1, degrees of randomness of 1.00 and 0.98 are obtained at 60 and 100 MHz, respectively, necessarily employing $A_{BN(2-3)}$ and eqs. (2) and (3) in each instance. Due to factors discussed above, these results may be about 7% low due to an underestimation of the i_1/i_2 ratio by eq. (2). In any case, previous interpretations at 60 MHz,^{5,6} which do not take account of the outside quartet peaks, would yield a B value of 0.92 rather than 1.00 when applied to the present data.

For the two-step polycondensation scheme employed, the ratio of glycol to terephthaloyl chloride in the first step fixes the sequence distribution in the ultimate copolyester. In the case of copolyester 1, the molar ratio used (0.5) results in an essentially random sequence of the comonomers. This must reflect the formation in the first step of a distribution of short NPG–TP homopolymer blocks, prior to the final condensation with BPA. The procedure used to prepare copolyester 2 differs only in the employment of a large excess of TPC in the sequence-determining first step. This results in the formation of a decreased proportion of homopolymer blocks of a size greater than the glycol diterephthalate and the anticipated high content of alternating (unsymmetrical) sequences in the final copolyester.

The authors are indebted to their colleagues at the Research Center, particularly J. G. Colson, J. H. Mackey, and V. A. Pattison, for constructive discussions pertaining to this investigation.

References

1. F. A. Bovey, *High Resolution NMR of Macromolecules*, Academic Press, New York, 1972, Chaps. III and X.
2. R. Yamadera and M. Murano, *J. Polym. Sci. A-1*, **5**, 2259 (1967).
3. T. S. Khramova, Ya. G. Urman, O. A. Mochalova, F. M. Medvedeva, and I. Ya. Slonim, *Polym. Sci. USSR*, **10**, 1040 (1968).
4. T. Harada and N. Ueda, *Chem. High Polym.* (Japan), **22**, 685 (1965).
5. F. L. Hamb, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 3217 (1972).
6. V. V. Korshak, S. V. Vinogradova, V. A. Vasnev, Yu. I. Perfilov, and P. O. Okulevich, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2209 (1973).

7. E. V. Gouinlock, H. W. Marciniak, M. H. Shatz, E. J. Quinn, and R. R. Hindersinn, *J. Appl. Polym. Sci.*, **12**, 2403 (1968).

8. F. A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, 1969, Chap. IV.

Received May 20, 1975

Revised July 11, 1975